This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

**Usage guidelines**

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.
+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.
+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.
+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

**About Google Book Search**

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

Library
of the
University of Wisconsin

Digitized by Google

University of Wisconsin Library

Manuscript Theses

Unpublished theses submitted for the Master's and Doctor's degrees and deposited in the University of Wisconsin Library are open for inspection, but are to be used only with due regard to the rights of the authors. Bibliographical references may be noted, but passages may be copied only with the permission of the authors, and proper credit must be given in subsequent written or published work. Extensive copying or publication of the thesis in whole or in part requires also the consent of the Dean of the Graduate School of the University of Wisconsin.

This thesis by..... has been used by the following persons, whose signatures attest their acceptance of the above restrictions.

A Library which borrows this thesis for use by its patrons is expected to secure the signature of each user.

NAME AND ADDRESS DATE

Digitized by Google

Digitized by Google

M3-01

Digitized by Google

Digitized by Google

Digitized by Google

Digitized by Google

# TITANIUM-SILICON ALLOYS

by

GEORGE EMERSON LONG

A Thesis Submitted for the Degree of

MASTER OF ARTS

UNIVERSITY OF WISCONSIN

1908

Digitized by Google

Digitized by Google

399116
OCT 13 1933
AWM
L 8515

# AN INVESTIGATION OF TITANIUM-SILICON ALLOYS.

Of late years, a great many compounds have been prepared by the use of the electric furnace, which previous to the employment of electricity as a heating agent, either could not be produced at all or could be produced only with the greatest difficulty on account of the high temperatures necessary for their formation. Among these, silicides of the various elements to the number of about forty have been prepared, many of which have been extensively studied. Up to the present time, however, the literature dealing with the silicides of titanium is scant, only two silicides having been prepared and they not studied completely.

The object of the work undertaken in this thesis was the production of titanium-silicon alloys from rutile by a single reaction in the electric furnace, and a study of the properties of the alloys so obtained. At the beginning of the work it was hoped that one or more of the three definite silicides of the formulae: $Ti_2Si$, $TiSi$ or $TiSi_2$ might be isolated.

## Literature.

Moissan in "Le Four Electrique" [1] states that

---

1. The Electric Furnace. Trans. by Lenher, p. 181.

Digitized by Google

Digitized by Google

the borides and silicides of titanium can be prepared in the electric furnace, in the fused or crystalline condition, and that they are as hard as diamond.

The first definite silicide of titanium mentioned in the literature, was prepared by L. Levy[2] by the action of $TiCl_3$ on silicon. The reagents were put in a porcelain tube brasqued by rutile, and heated in a blast furnace. Crystals of an arborescent form were obtained which on analysis proved to be of the formula $Ti_2Si$. Two analyses of the material gave the following results: (1) Ti 76.14% Si 22.69% and (2) Ti 77.21% Si 20.90%. The theory for $Ti_2Si$ is Ti 77.2% Si 22.8% so Levy concludes that he has obtained the silicide $Ti_2Si$. He prepared only a few centigrammes of this substance. Beyond the statement that the crystals were of an arborescent form there is no information given as to the properties of this compound.

The next contribution to the subject of titanium silicides was made by Hönigschmid[3]. He claims to have prepared the compound $TiSi_2$. The charge used, was made up as follows: 200 grams powdered aluminum, 250 grams sulphur, 180 grams fine sand and either 15 grams titanic acid or 40

---

2. C.R. 121; 1148-1150 (1895) Abstr. Ch. Soc. Journal Part 2; 304 (1896)
3. C. R. 143; 224-226 (1906) Abstr. Ch. Soc. Journal 90; Pt. 2; 678 (1906)

Digitized by Google

Digitized by Google

grams titanium potassium fluoride. This was put in a Hessian crucible, covered with a thin layer of powdered magnesium and ignited by means of a Goldschmidt pastille. The observed properties of the product obtained are given in the following statements: Titanium silicide, $TiSi_2$ crystallizes in small iron-gray, tetragonal pyramids having a hardness of 4-5 and a specific gravity of 4.02 at 22°C. It oxidizes with difficulty, but burns in chlorine below a red heat. It is insoluble in all mineral acids except hydrofluoric, but dissolves slowly in 10% KOH solution. Fused KOH reacts vigorously on it at a red heat, but $KHSO_4$ is without action under these conditions. Hönigschmid gives the analysis of two samples of material as: (1) Ti 45.9% and (2) Ti 45.6%. He took Si by difference. The theory for $TiSi_2$ is Ti 45.85 percent Si 54.15 percent.

## Electric Furnaces.

In the experimental work, three types of electric furnace were used, viz. the granular carbon resistor furnace the horizontal arc furnace and the vertical arc furnace. The source of current for most of the work was a direct current 110 volt dynamo, rated at 825 amperes. An alternating current was also used on a few occasions.

The resistor furnace most frequently used was a

Digitized by Google

Digitized by Google

rather small one, its usual dimensions being: 8 3/4 inches long, 3 inches wide and 4 inches deep, though these were slightly varied from time to time. The side walls were lined with whole magnesia brick while the ends were built up of fragments of magnesia brick. The electrodes were of round Acheson graphite 1 1/2 inches in diameter. These extended into the furnace about 1 inch, and pieces of graphite were laid around the ends to give a larger conducting surface, to make the heating more uniform. In running the furnace, a shallow layer of granular carbon resistor was first put in the bottom, then the crucible or crucibles put in and resistor shoveled in around them. The furnace was strengthened by a layer of firebrick outside which also served as a heat insulator. A platform of firebrick having a ventilated base, supported the furnace. Such a base is shown in the picture of the arc furnace, Figure 1.

The Horizontal Arc Furnace was originally built for experimenting on the production of metallic titanium but later was used almost exclusively for making the silicide. The interior was lined with magnesia. The two side walls were built of two magnesia bricks set on edge on a foundation of broken pieces of magnesia, mostly halfbrick, and all cracks were filled with a cement made of magnesia and waterglass. The waterglass was used quite dilute as

Digitized by Google

Digitized by Google

otherwise the magnesia would be badly fluxed. The ends were built of pieces of magnesia brick and magnesia cement. The electrodes were of 1 1/2 inch Acheson graphite. In building up the ends, the electrodes were first put in their holders and brought into position in the furnace. They were wrapped in heavy paper to prevent their being fastened in the cement and the ends were built up around them.

After the cement was dry, the electrodes could be moved in or out without disturbing the ends of the furnace, and if mostly fragments of brick and very little cement were used the ends remained in good condition for several runs. However, after a time the holes became too small, due to the outside of the electrodes gradually burning off, where they entered the furnace, allowing the magnesia to settle closer around them, so that it was impossible to feed them in and even to withdraw them in some cases. The holes then had to be enlarged and usually the ends above the electrodes rebuilt. To diminish oxidation of the electrodes outside of the furnace, they were painted with a mixture of carborundum powder and dilute waterglass solution. This was found quite beneficial. The inside dimensions of the first furnace were 4 1/2 inches square and 3 1/2

Digitized by Google

Digitized by Google

inches deep. In later furnaces these were increased to 5 inches square and 6 inches deep. The furnace was covered outside of the magnesia lining with firebrick. The outside dimensions of the furnace were 18 inches square and 7 1/2 inches high, while the base was 13 3/4 inches high. Figure 1 is a photograph of the arc furnace used.

In the first run, the furnace was covered with two magnesia bricks. After the run they were badly cracked so it was found necessary to get a better material. Some carborundum brick had just been received by the department and it was thought that possibly these might be suitable for furnace covers. But owing to the large amount of fire clay in them they fused badly on the lower side and so had to be discarded.

An attempt was then made to make a cover of magnesia. For this purpose a mold was constructed using as a bottom a carbon plate 12 inches square. The sides were of pasteboard. The magnesia was a mixture of equal parts of electrically shrunk and red magnesia. A layer of this 1 inch deep was put in the mold dry, then a piece of pasteboard was put on, then another layer of magnesia until three were put in. It was hoped to get three good covers. A carbon cover of the same dimensions was then put on, and resistor filled in around the mold. The heating was done in a large resistor furnace. The resistor became bright red but

Digitized by Google

Digitized by Google

the magnesia was not baked. The bottom of the mold should have been set higher and the resistor heated almost white hot. The next time a mold entirely of graphite was used. It was made for two bricks the size of a fire brick. To separate the bricks two sheets of heavy paper were used, which were kept in place by a sheet of tin, till the magnesia was filled in. The mixture of magnesia was the same as before, with the addition of a small amount of $BaCO_3$ to aid in cementation. This time the bricks baked quite well except for a little softness along one edge. They were placed on the top of the arc furnace and heated about 20 minutes with 200 amperes at 100 volts at the end of which time they were so badly cracked as to fall to pieces when moved. It was concluded, therefore, that magnesia covers for the arc furnace were a failure. A graphite cover finally had to be resorted to, and this was found to last quite well if kept well covered with magnesia. Unless the electrodes are pointed there is difficulty in starting the furnace, as the arc repeatedly snaps out. The positive electrode had to be re-pointed before each run, as it assumed very irregular shapes, but the negative electrode kept its conical form very well and seldom needed re-pointing.

The first furnace lasted for nine runs;the next

Digitized by Google

Digitized by Google

one with slight repairs lasted for twenty runs. It was found satisfactory to fill the furnace partially with a magnesia containing considerable carbonate. The lining containing the charge was bedded in this and the product was easily removed from the furnace as a cold chisel was needed only to loosen it from the walls. It also prevented contamination of the product in case it went through the bottom of the lining. The furnace was strapped with two iron bands to prevent the bricks spreading.

The observation was repeatedly made that with a current of 500 amperes at 80 volts after about 20 minutes the arc could not be maintained steady, and to do so a lower voltage had to be used. It seemed as though the gases rising broke the arc. It was thought that the flaming arc might work better so the electrodes were soaked in a saturated solution of $CaCl_2$ for two days, but there was no improvement in the maintenance of the arc.

A vertical arc furnace was used in an attempt to prepare larger quantities of silicide than could be handled in the other furnaces. The first one built was lined with magnesia brick and was 4 inches square and 8 inches deep inside. A flat graphite electrode served to conduct the current in, and also as a bottom. The upper electrode was

Digitized by Google

Digitized by Google

a 1 1/2 inch round graphite rod. The magnesia was badly fluxed, either by the rutile or the silica formed, or both.

The furnace was next lined with graphite slabs and the corners filled with a cement of graphite dust and dilute waterglass. This cement held well so that in no case did fused material leak from the furnace. Its dimensions were now 4 1/2 x 4 x 8 inches. Outside of the graphite slabs were placed magnesia brick, and outside of these, firebrick. Difficulty was occasionally experienced from the upper electrode freezing into the charge. In these cases the electrode was raised taking the carbon box along with it so that an arc was started between the lower electrode and the bottom of the furnace. At the same time a gentle pressure was exerted on the sides and by this means the electrode was released. Some trouble was also caused by the arc playing between the upper electrode and the sides of the furnace; so the furnace was made slightly larger, 5 x 5 x 8 inches. There was still some arcing to the side, but not so badly as before.

## Experimental Work.

The experimental work was begun in November 1907 and continued into April 1908. It consisted of over 60 furnace runs, a considerable amount of analytical work, to-

Digitized by Google

Digitized by Google

gether with a great deal of work preparatory to the real experiment, such as furnace building, the making of graphite crucibles, molding and baking magnesia linings for the crucibles, grinding the materials to be used in the charge and separating the iron from them by an electromagnet. The furnace runs, each required a great amount of time since, in general only one could be made in the same furnace the same day owing to the long time required for cooling. Each analysis also involved a considerable outlay of time.

The source of titanium was the mineral rutile which usually contains from 90--100% $TiO_2$ and a small amount of iron. In a few of the first experiments a dark brownish black variety of rutile was used, but was soon discarded as being too impure and a much better grade of a reddish color was henceforth employed. This contained comparatively little iron but for each run this iron was magnetically separated. As a source of silicon and as reducing agents elemental silicon and carborundum were used. To aid in the reduction, carbon, calcium, calcium carbide, and aluminum were also tried.

Titanium-silicide by reduction with carbon and silicon.

This charge was made up according to the follow-

Digitized by Google

Digitized by Google

ing equation:

$$2\ TiO_2 + Si + 4C = Ti_2Si + 4\ CO$$

The charge was put in a 2 inch graphite crucible and heated for 40 minutes in the small resistor furnace. The average power was 20 kilowatts. The furnace heated evenly and got very hot. The product after cooling was a metallic looking mass. It was very hard, cut quartz easily and seemed to make faint scratches on corundum, but this was difficult to decide. The product is probably the silicide considerably carbonized. This material together with additional charge of the former proportions was again treated. The furnace did not get so hot this time, the average K.W. being 13.9, and the product was about two-thirds nitride, $Ti_2N_2$. It seems that if the temperature is not carried high enough, nitride forms instead of silicide.

The next attempt was to make TiSi.

$$TiO_2 + Si + 2C = TiSi + 2CO.$$

The furnace was run quite hot. An average power of 18.9 K.W. was used. The product was a light colored metallic mass and contained no nitride. Much carbon must have been dissolved in it as the effect of capillary action could be seen and the crucible was badly attacked. The results seem to show that with the furnace used, an average power of

Digitized by Google

Digitized by Google

about 18 K. W. is needed to produce the silicide. With 13.9 K. W. practically no silicide is formed.

Later two runs were tried in the arc furnace according to the equation:

$$TiO_2 + 2Si + 2C = TiSi_2 + 2CO$$

The charge was heated in a shallow magnesia lining, using 500 amperes at 80 volts for 20 minutes. Then the voltage was lowered to 55 for 5 minutes. The product looked as though the silicon had vaporized and left mostly titanium, but a test failed to reveal free titanium though the percentage of combined titanium was probably very high. The material was non-crystalline and very hard to break. 90 grams of product were obtained. The next run was made to see whether less heating would give a product with more silicon in it. 500 amperes at 80 volts were used 15 minutes. The product was much the same, but complete reduction had not occurred, showing the necessity of heating about as before.

## Graphite block experiment.

In one of the early experiments, four holes were drilled in a block of graphite and charges put in them as follows: 12 grams rutile and 6.3 grams silicon; 8 grams rutile and 3.6 grams silicon; 12.4 grams $Ti_2N_2$ and 5.6 grams

Digitized by Google

Digitized by Google

silicon; and 12.4 grams $Ti_2N_2$ and 2.4 grams carbon. The purpose was to see whether carbon and silicon can each drive nitrogen from combination and whether silicide or carbide forms at the lower temperature. The block was heated in the resistor furnace for an hour. The charges containing silicon were both almost completely converted to silicide; those containing carbon gave a product of dark material containing some bright specks, probably carbide.

The experiment seems to show that carbon and silicon can each replace nitrogen, also that the silicide is formed at a lower temperature than the carbide.

Titanium-silicide by reduction with carborundum.

A charge consisting of 80 grams rutile and 30 grams carborundum was put in a 2 inch graphite crucible and heated in a resistor furnace for 40 minutes with an average power of 20 kilowatts.

The product contained some lumps of silicide but much of the carborundum seemed to have been driven off by high heating. The product with additional charge was again heated, but more gradually, the energy record being

Digitized by Google

Digitized by Google

| Amperes | Volts | K. W. | Time | |
|---|---|---|---|---|
| 70 | 75 | 5.25 | 0 | minutes |
| 130 | 65 | 8.45 | 6 | " |
| 250 | 45 | 11.25 | 16 | " |
| 310 | 45 | 13.95 | 25 | " |
| 400 | 45 | 18.00 | 40 | " |
| 500 | 51 | 25.50 | 45 | " |
| 350 | 55 | 20.25 | 48 | " |
| 280 | 57 | 15.96 | 57 | " |
| | Shut down | | 65 | " |

The total energy was 15 K. W. hours. The product was a light colored metallic looking mass.

Neumann [4] states that in order to reduce metallic oxides with carborundum, sodium carbonate must be used as a flux. To try this, two charges were made up, one containing $Na_2CO_3$. Graphite crucibles were used and the heating was done in a resistor furnace. The heating was insufficient, for in the crucible which had contained $Na_2CO_3$ very little reduction had occurred, and in the other crucible the product was mainly nitride with small amounts of silicide.

Later some runs were made with the arc furnace.

---

4. Ch. Soc. Jour. 80; Part 2; 98 (1901)

Digitized by Google

Digitized by Google

$$2\ TiO_2 + 2CSi = Ti_2Si + 2CO + SiO_2$$

250 grams rutile and 125 grams carborundum were heated in a shallow magnesia lining with a current of 500 amperes at 80 volts for 22 minutes. The product was mostly nitride with some light colored globules; presumably silicide.

Next a charge was made up according to the equation

$$TiO_2 + 2CSi = TiSi + 2CO$$

150 grams of rutile and 150 grams of carborundum were heated with an arc of 500 amperes at 80 volts for 10 minutes, then the voltage was reduced to 60 and kept there for 15 minutes. Again the product was mostly nitride with a little silicide.

Finally a charge was made up using $Na_2CO_3$

$$2\ TiO_2 + 3\ CSi + Na_2CO_3 = 2\ TiSi + Na_2SiO_3 + 4\ CO$$

It consisted of 100 grams rutile, 75 grams carborundum and 66 1/4 grams $Na_2CO_3$. 500 amperes at 85 volts were used for 20 minutes. The furnace gave out a great quantity of smoke and bright white flames and got very hot. The product seemed to be unreduced material and contained no metallic material whatever.

It seems as though silicon can not be made to go into combination with titanium in any considerable quantity when CSi is used as a reducing agent. Especially is

Digitized by Google

Digitized by Google

this true in using the arc furnace, since fair results were once obtained with the resistor furnace.

It appears also that the sodium carbonate instead of aiding in the reduction, had hindered it, probably by oxidizing the silicon.

## Titanium-silicide by reduction with silicon and calcium.

Four runs were made using calcium to aid in the reduction, but as the results were not very promising either from the standpoint of yield or appearance, experiments using calcium were discontinued. A resistor furnace was used in each case. The calcium did not produce a violent action as it does in some reductions. Only small globules of a metallic looking product were obtained.

An interesting observation was made however in connection with one run. When the small metallic fragments were treated with HCl they dissolved in part and gave a violet colored solution showing that instead of the silicide,metallic titanium had been produced.

## Titanium-silicide, by reduction with silicon and calcium carbide.

$$3\ TiO_2 + 3\ Si + 2\ CaC_2 = 3\ TiSi + 2\ CaO + 4\ CO$$

40 grams rutile, 20 grams $CaC_2$ and 31.5 grams silicon were

Digitized by Google

Digitized by Google

put in a graphite crucible and heated in a small resistor furnace for 45 minutes. A great deal of metallic material was obtained which consisted of titanium and calcium silicides. When treated with HCl the following reaction took place:

$$CaSi_2 + 2\ HCl = CaCl_2 + Si_2H_2$$

Titanium silicide was left as a metallic looking powder and the silicon hydride as a yellowish powder. When this residue was treated with 20% KOH solution the following reaction occurred:

$$Si_2H_2 + 4\ KOH + 2\ H_2O = 2\ K_2SiO_3 + 5\ H_2$$

After treating with HCl and then with KOH solution, an analysis of the metallic powder left, was made, giving Ti 54.91% and Si 45.09%. This is lower in titanium than theory for TiSi and higher than for $TiSi_2$. It more nearly approaches the titanium content of $Ti_2Si_3$ which is 53.03%.

## Titanium-silicide using silicon, aluminum and sulphur.

$$4\ Al + 10\ S + 8\ Si + 4\ TiO_2 = 4\ TiSi_2 + 4SO_2 + 2Al_2S_3$$

An attempt was first made to carry out the reaction by the alumino-thermic process, using 13.5 grams of coarsely powdered aluminum, 28 grams silicon, 40 grams sulphur and 40 grams rutile. The igniter was a mixture of

Digitized by Google

Digitized by Google

magnesium and barium peroxide. The charge was put in a clay crucible covered outside and inside with magnesia. It was ignited by means of a magnesium ribbon. Only a superficial layer was acted on. The same charge was afterward heated in the resistor furnace till a reaction occurred, but only a few small metallic looking lumps were formed. The experiment was not repeated.

Silicide using silicon as reducing agent.

The first attempt to produce the silicide by using silicon alone as a reducing agent was described before in connection with the graphite block experiment. The result was promising but no more experiments were carried out for a time as it was desired to try some other experiments first. When this method was again resumed the attempt was first made to get the highest silicide $TiSi_2$ according to the equation:

$$TiO_2 + 3\,S = TiSi_2 + SiO_2$$

It was decided to discontinue the use of graphite crucibles in this and subsequent runs on account of the very obvious contamination of the product by carbon, so the heating was done under the arc in a shallow magnesia lining. The charge consisted of 60 grams rutile and 93 grams silicon. This included an excess of 30 grams of silicon as it was thought

Digitized by Google

Digitized by Google

that a great deal might distil out. The magnesia lining which held the charge was 4 inches in diameter and 3 inches high, outside measurements. A current of 500 amperes at 80 volts was employed for 15 minutes. Bright vapors began to come off, which were taken for silicon vapor so the furnace was shut down. The product was a light colored material somewhat resembling silicon. It was unacted on by hydrochloric, nitric or sulphuric acids but dissolved vigorously in cold concentrated hydrofluoric; cold 10% KOH solution acts on it rapidly. The mass weighed 70 grams which was a yield of 89% of the calculated amount. An arborescent crystalline form could be distinguished in some parts of the product. A specimen was polished and etched with hydrofluoric acid. Figure 2 is a microscopic photograph of it magnified 37 diameters. A considerable amount of unattacked material seems to be present, however an analysis showed only 10.64% free silicon. The percentage of titanium found was 35.58 and the combined silicon 53.78. The specific gravity is 3.77 at 22°C.

Another run was made using exactly molecular proportions for $TiSi_2$; 120 grams rutile and 126 grams silicon were heated with an arc of 500 amperes at 80 volts for 15 minutes. An ingot weighing about 160 grams was obtained. Allowing for a little slag the yield was about the calculated amount. Two distinct colors were noted in the product ,

Digitized by Google

Digitized by Google

one rather metallic as though much of the silicon had distilled out, the other more resembling silicon. On breaking up the ingot a well marked crystalline form was discovered. This is shown, magnified 7 diameters, in Figure 3. The form could also be seen in the product of the preceding run but, not so well.

It will be remembered that Levy described the silicide $Ti_2Si$ as having an arborescent crystalline form. No analysis of this specimen was made, but the appearance of the greater part of it was the same as that of the former product. It seems strange that in this specimen so high in silicon the same crystalline form should be found as that ascribed to the lowest silicide $Ti_2Si$. The action of reagents on it was the same as on the other except that cold KOH did not seem to act so readily, but hot KOH solution acted vigorously. Its specific gravity was 3.92.

A charge was next made according to the equation:

$2\ TiO_2 + 3\ Si = Ti_2Si + 2\ SiO_2$ , using 180 grams of rutile and 94.5 grams of silicon. This was heated by 500 amperes at 80 volts for 20 minutes. An interesting product was obtained, which was lighter colored and looked less like silicon than the former products. It weighed 138 grams which was a yield of about 95% theory. On breaking it open, small needle-like crystals were found which under the microscope proved to be hexagonal prisms. Figures 4 and 5

Digitized by Google

Digitized by Google

show some crystals from this charge. By close observation, the hexagonal form can be seen, especially in the two crystals forming the "V" at the top of Figure 4. A sample of partly crystalline and partly non-crystalline material was analysed giving Ti 58.52% and Si by difference 41.48%. On purely crystalline material, cold concentrated hydrofluoric acid acted vigorously; hydrochloric, nitric sulphuric and nitrohydrochloric acids had no action, and hot saturated KOH solution seemed without action although it acted on the non-crystalline matter. Its hardness lies between 8 and 9, as it cuts quartz easily and seemed to slightly scratch corundum; but this could not be fully decided. Its specific gravity was 4.26 at 22°C.

Hoping to get a larger mass in which more crystals might be obtained a charge was next prepared in accordance with the equation:

$$TiO_2 + 2\ Si = TiSi + SiO_2$$

320 grams rutile and 224 grams silicon were used. Instead of a magnesia lining some of the purest magnesia was put in the furnace, dampened and molded to form a cavity in which the charge was put. The charge was heated 30 minutes with an average amount of energy of 30 kilowatts. Crystals like those of the former product were obtained. The product weighed approximately 125 grams, which was a yield of about 39%. The heating was probably not long

Digitized by Google

Digitized by Google

enough for this size. The specific gravity of the product was 4.67.

Two runs were made for $Ti_2Si$ with the addition of copper as a crystallizing medium. Enough excess of silicon was put in to form $Cu_2Si$ to prevent the copper robbing the charge of silicon. By using copper as a crystallizing medium no free titanium or silicon should be present in the silicide. In the first case the heating was too high and not much copper was left in the charge. In the second trial the heating was lower. The product was a light colored material. It was very dense indicating the presence of much copper. One piece was made anode in an electrolytic cell with 25 c.c. nitric acid in 500 c.c. water as electrolyte. This was treated for several days, but the method of purification did not seem very good as solution was very slow, and the silicide which dropped off still contained much impurity.

Another specimen was finely ground and treated with dilute nitric acid. This time much trouble was found in freeing the titanium silicide, first, from gelatinous silica, and later, from the last traces of $Cu_2Si$. No analysis was made of this material as it could not be completely purified and some more promising material was taken

Digitized by Google

Digitized by Google

for analysis at this time.

Nine more runs were made, in all but one of which charges were used, made up according to the equation for $Ti_2Si$, the other was fof $TiSi_2$. In every case more or less of the needle like crystals were obtained though in the run for $TiSi_2$, other conditions being the same, one might expect the arborescent crystalline form mentioned before. The weight of the charge was the same, and the furnace was practically the same size. The heating was for 30 minutes with an average amount of energy of 32 K. W. Although the intensity of the heating was not so great the total amount of energy was greater, also what was quite important, the furnace being new in this run, was nearly air tight, so holding the heat in well. The product obtained in this case weighed 64 grams.

In the runs for $Ti_2Si$ the charges usually consisted of 200 grams rutile and 105 grams of silicon. The yields obtained vary from 40% to 100% of theory, the average being about 70%.

The conditions of heating giving the maximum yield could not be decided on for narrow limits; however some general information can be given. With a horizontal arc furnace of the dimensions stated and with a charge of

Digitized by Google

Digitized by Google

about 300 grams, at least an amount of heat equivalent to that furnished by 27 kilowatts for 20 minutes must be employed to give a fair yield, 60% to 70%. The experiments, in general go to show that higher heating in most cases gives better results. No upper limit of allowable heat was observed for in every case, when using an arc of 500 amperes at 80 volts, after from 15 to 20 minutes the arc could no longer be maintained as stated before, due presumably to the breaking of the arc by the hot gases arising.

After this series of runs, some material was taken from each, making altogether 314 grams. This was melted under the arc.

| Current | E. M. F. | Time. |
|---|---|---|
| 300 amp. | 90 volts | 15 minutes |
| 300 " | 80 " | 3 " |
| 300 " | 65 " | 12 " |

A chunk of silicide weighing 250 grams was obtained. This contained some good crystals, a photograph of which is shown in Fig. 6. The magnification is 7 diameters. An analysis of mostly crystalline material together with some non crystalline which could not be freed from it gave Ti 54.13%. The action of reagents was the same as in the former cases. The material scratched quartz easily. Three pieces were

Digitized by Google

Digitized by Google

tested as to specific gravity and gave the values: 4.705, 4.72 and 4.73 at 22°C.

After this melt two more runs were made in the horizontal arc furnace for $Ti_2Si$. In the first no lining was used but a hollow was again formed in the loose magnesia. The charge was 400 grams rutile and 210 silicon. The total energy used was 18 K. W. hours. The weight of the product was 239 grams. The product was a very uniform material, containing but few crystals, and appeared to be low in silicon. The yield was 77% of theory. An analysis showed 64.57% Ti, a little higher than theory for TiSi which contains 62.87% Ti.

In the second run, 200 grams rutile and 105 grams silicon were put in a lining and heated with a total of 17 K. W. hours. The time of heating was 40 minutes. In this case a still more uniform product was obtained.

Following these two runs, five were made in the vertical arc furnace. In the first case, the furnace was lined with magnesia brick. The charge was 1600 grams rutile and 840 grams silicon. Several minutes were spent, starting the furnace with a low voltage. Then the heating was continued for 17 minutes with an average of 33 K. W. The product contained considerable quantities of crystalline and

Digitized by Google

Digitized by Google

non crystalline material weighing altogether about 400 grams. Much unreduced charge was also present. Some crystalline matter is shown in Figure 7. The furnace had to be shut down sooner than it was intended, because having fluxed the bricks the fluid matter was rapidly leaking out.

In the next run the furnace was lined with graphite slabs. The charge contained 3200 grams rutile and 1680 grams silicon. As before the furnace was started with a low voltage then the energy record was as follows:

| Amperes | Volts | Time |
|---|---|---|
| 300 | 60 | 25 minutes |
| 500 | 55 | 20 " |
| 300 | 75 | 15 " |

The total energy was 22 K. W. hours. The charge was covered with silica. About 700 grams of silicide was obtained, in which were some very fine crystals. Much unreduced matter was found in the product; the charge seemed not fusible enough.

On the basis of an analysis of some of this crystalline material, the writer first came to the conclusion that he had prepared a new silicide of titanium corresponding to the formula $Ti_2Si_3$. The calculated amount of titanium in this compound is 53.03%, and an analysis gave the

Digitized by Google

Digitized by Google

percentage of titanium as 52.85, a difference of only 0.18%. This difference may easily be explained from the fact that owing to the minuteness of the crystals, in no case could any considerable quantity of them be obtained entirely free from non crystalline matter. However in this run a much greater quantity than usual was obtained so that the sample for analysis was a very good one.

In an earlier analysis where the crystals were not so clean the percentage of titanium was found to be 54.13, a difference of 1.10% from theory. It will also be remembered that the formula $Ti_2Si_3$ was suggested for the silicide obtained by reduction with calcium carbide and silicon. In this case the percentage of titanium was 1.88% higher than the calculated amount. In still another analysis titanium was found to be 54.61% a difference from theory of 1.58%. The results of these analyses, together with the crystalline form which differs from that of either of the silicides previously prepared, led the writer to the conclusion that he has demonstrated the existence of a new silicide.

Some pictures of crystalline matter from the last run are shown in Figures 8 and 9. In Figure 8 the magnification is only 7 diameters, while in Figure 9 it is 37 diameters. The product obtained in this last case was treated

Digitized by Google

Digitized by Google

again using fluorspar as a flux. This was first melted and the charge fed in. The product was not homogeneous, as the slag was too infusible. A slag of silica, fluorspar and lime was then made and the product again treated but with no better results. The fumes of hydrofluoric acid given off by the electrolysis of fluorspar were extremely disagreeable.

A new charge was made up like the last one and a slag of lime, silica, and fluorspar prepared. The heating lasted for 1 hour and 46 minutes with an average of 23 K. W. The slag was very fluid but the silicide was badly mixed through the slag.

Digitized by Google

Digitized by Google

## Analytical Method.

The analytical method used was as follows: .2 to .3 grams of silicide was weighed out into a platinum crucible some water and several drops of sulphuric acid added. Then hydrofluoric acid was added drop by drop until the solution was complete. The action being quite vigorous, it was necessary to keep the crucible covered during the addition of the acid. After the action had ceased, the crucible was placed in an electric heater where the hydrofluoric acid soon evaporated. The residue was then dissolved in water and transferred to a weighed porcelain crucible and evaporated practically dry in the electric heater, then placed on a triangle over a sand bath and heated till most of the fumes had been driven off. The last traces of fumes were carefully driven off over a Bunsen burner and finally the crucible was heated in the blast and weighed. The contents of the crucible were weighed as $TiO_2$. Due to the variation in the results of analysis, it was first thought that some titanium must have been driven off as fluoride along with the silicon, however several authorities say that no titanium will be lost if sulphuric acid is present. But it will also be remembered that the specific gravities of various samples also differed considerably and even different samples from the same run differed slightly in specific gravity.

From these facts it was concluded that the non-

Digitized by Google

Digitized by Google

crystalline matter is of varying composition and to its presence is due the irregularities in the analyses of the crystalline matter.

## Experiments on the production of titanium.

Simultaneously with the experiments for making the silicide a few were undertaken for the production of metallic titanium. Accounts of the various attempts to produce titanium are so common in the literature that no review of them will be given. The main difficulty seems to be the great affinity between titanium and nitrogen.

In the first experiment, a shallow graphite crucible was used; itd dimensions being 4 x 1 3/4 inches. The charge consisted of 24 grams rutile, 24 grams calcium, 16 grams of aluminum and 28 grams of sulphur. The horizontal arc was used and the heating was for 16 minutes with 500 amperes at 80 volts. Only some small metallic specks were found in the product, and no free titanium was found. When treated with hydrochloric acid the product gave off $H_2S$.

For the next run a charge consisting of 31 grams rutile, 7 grams calcium and 20 grams powdered aluminum was made up. It was heated for 10 minutes with 500 amperes at

Digitized by Google

Digitized by Google

80 volts. A shallow graphite crucible lined with magnesia was used. The product contained a small amount of metallic material which gave a test for aluminum and calcium but no free titanium.

The next charge contained 50 grams rutile, 4 grams magnesium, 9 grams aluminum (powdered) and13 grams of calcium shavings. The charge was covered with fluorspar and heated for 10 minutes with 500 amperes at 90 volts. A small quantity of a light colored metal was obtained which in HCl gave a bluish solution, showing the presence of free titanium.

Neumann[5] tried to reduce rutile by silicon according to the equation:

$$TiO_2 + Si = Ti + SiO_2$$

He obtained a gray-white, very brittle metal which was very hard to separate from the slag. He found 2.99% of iron and 20.37% of silicon in it. He says that silicon has an affinity for titanium equal to that of carbon. He suggests heating the product again with more rutile, in which case the silicon could be removed. Before the article appeared a run had been tried according to this equation. The charge

---

5. Zeit. für El. Chem. 14; 171; (Apr. 1908)

Digitized by Google

Digitized by Google

was 200 grams rutile and 70 grams silicon. It was heated in a shallow lining with an arc of 500 amperes at 80 volts for 15 min., then 400 amperes at 65 volts for 10 minutes. A light colored material containing many needle like crystals was obtained. No free titanium was detected. It seemed to be the same as the product obtained in attempting to make the silicide.

Later, an alloy of 50% Al, 30% Ca and 20% Mg was used in an attempt to reduce rutile. Attempts to ignite the charge by the Goldschmidt method failed, but when a charge of 189 grams rutile and 103 grams alloy were heated under the arc with 500 amperes at 80 volts for 8 minutes a few metallic globules were obtained, which gave a violet solution with HCl, proving the presence of free titanium. However the nitride was present in large quantities, showing the difficulty in preparing titanium in the presence of air.

Digitized by Google

Digitized by Google

## Conclusions.

1. The existence of a new silicide of titanium has been indicated.

2. Titanium-silicon alloys can be best prepared by using silicon alone as a reducing agent and source of silicon.

3. The non-crystalline matter of the various products consists of alloys of varying composition, shown both by analysis and specific gravity determinations.

4. The amount of silicon in the charge influences the character of the product.

5. The time, as well as the intensity, of heating plays an important part in determining the character of the product.

6. For large amounts of silicon, with heating of short duration or of low intensity, the arborescent crystalline form, together with the non-crystalline material resembling silicon but of finer fracture, make their appearance.

7. With longer heating or greater intensity the crystals consisting of hexagonal prisms appear, and the non-crystalline material is of a light color.

Digitized by Google

Digitized by Google

8. With still higher and longer heating, a still lighter colored, more uniform and less crystalline product is obtained.

9. The higher the heating the lower the silicon content becomes.

10. The average yield was about 70% of theory.

11. The hardness of the silicide lies between 8 and 9. It is practically the same for all specimens tested. This is harder than given by Hönigschmid but not so hard as Moissan states it to be.

Digitized by Google

Digitized by Google

## Bibliography.

### Text Books.

Moissan-- Lenher The Electric Furnace 178-184 (1905)

Browning-- Rarer Elements, Intr. to, 58-65 (1903)

Ohly-- Rare Metals, 165-174 (1903)

Watt-- Dictionary of Chemistry 4; 737-751 (1902)

### Periodicals.

1890-- De l'action du chlorure de titane sur les metaux. L. Levy C. R. 110: 1368-1370

1895-- Sur le titane cristallise' et les combinaisons de titane et de silicium. L. Levy C. R. 121: (1148-1150)

1897-- Production of titanium. H. Moissan U. S. P. 591, 355 (Oct.)

1901-- Calcium carbide and silicon carbide as reducing agents for metallic oxides. B. Neumann. Ch. Soc. Jour. 80: Pt. 2; 98.

1903-- Reduction of titanium oxide with aluminum. Rossi. E. & M. I. 1: 523.

1904-- Production of titanium and its alloys. Huppertz. Metallurgie Nos. 17-22 Abstr. E. & M. I. 3: 35 (1905)

Digitized by Google

Digitized by Google

Bibliography concluded.

1905-- Reduction of titanium oxides by aluminum. U. S. P. 802, 941 (Oct.)

1906-- Sur le silicure de zirconium Zr $Si_2$ et le silicure de titane Ti $Si_2$. O. Hönigschmid. C. R. 143: 224-225.

1907-- Réduction of titanium and other oxides. Becket. U. S. P. 858, 329 (June)

1908-- Silicium als reduktions mittel für die oxyde schwer schmelzbarer metalle. B. Neumann Zeit. für El. Ch. 14;169

Digitized by Google

Digitized by Google

Figure 1.

Digitized by Google

Digitized by Google

Figure 1.

Digitized by Google

Digitized by Google

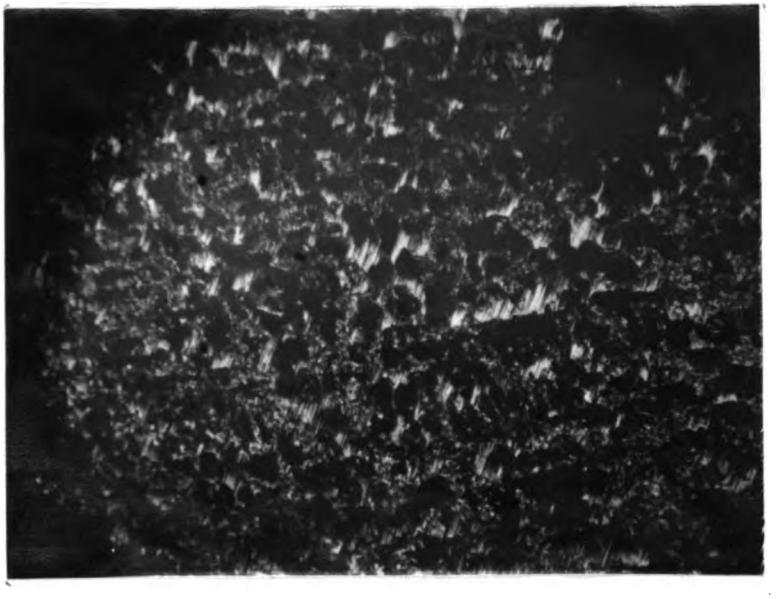

Figure 2.

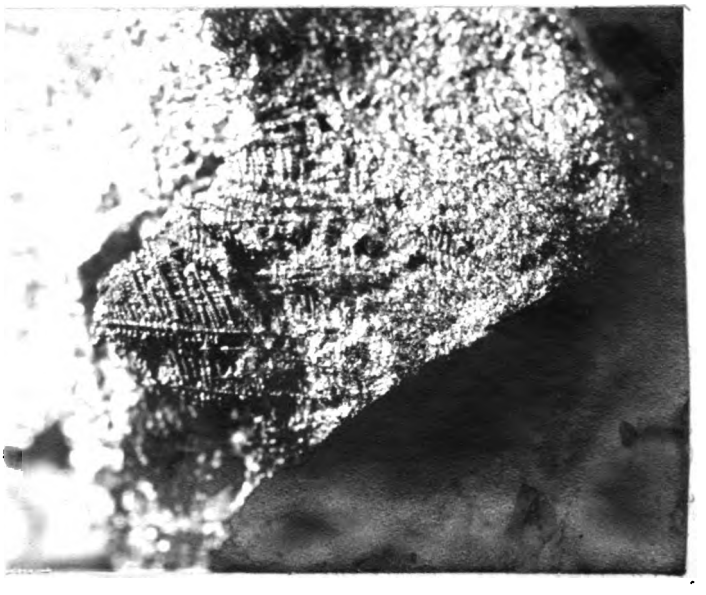

Figure 3.

Digitized by Google

Digitized by Google

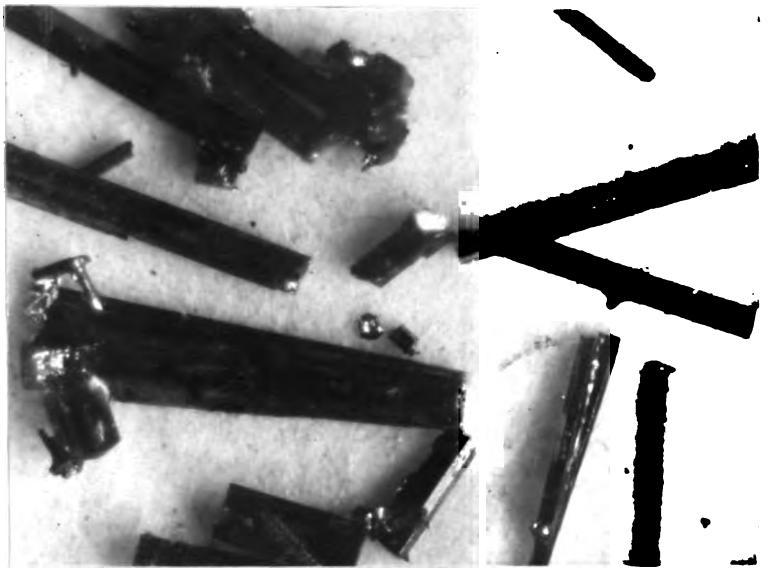

Figure 4.

Figure 5.

Digitized by Google

Digitized by Google

Figure 6.

Figure 7.

Digitized by Google

Digitized by Google

Figure 8.

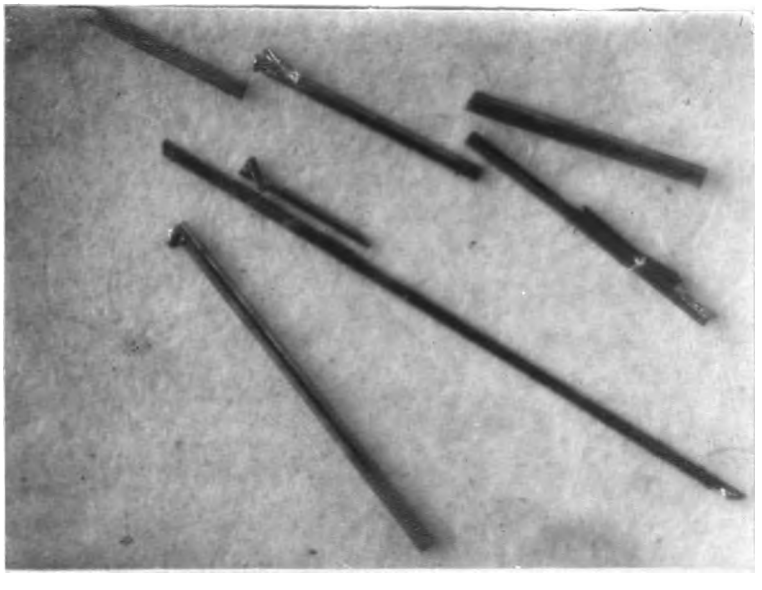

Figure 9.

Digitized by Google

Digitized by Google

Approved:

C. F. Bingham

Professor of Applied Mathematics

Digitized by Google

Digitized by Google

Digitized by Google

Digitized by Google

Digitized by Google

89086881281

b89086881281a

Digitized by Google